Effect of Laser Wavelength on the Formation of Al2O3-TiO2 System Thick Films by Laser Chemical Vapor Deposition

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論 文 内 容 要 旨

Chapter 1 Introduction

Al_2O_3-TiO_2 system thick films have been used in several applications (Al_2O_3 film: wear-resistance protective coating; TiO_2 film: photoctalyst and optical coating; Al_2TiO_5 film: thermal-shock protective coating) due to its excellent properties (Al_2O_3: high hardness, oxidation resistance and high temperature stability; TiO_2: photocatalytic, photovoltanic and optical properties; Al_2TiO_5: high thermal shock resistance, thermal insulation and low thermal expansion). Laser-assisted chemical vapor deposition (Laser CVD) can be a candidate technique for preparing Al_2O_3-TiO_2 system thick films because of the superior conformal coverage and microstructure controllability in high deposition rate. Laser CVD can be basically categorized into two types, i.e. photolytic laser CVD and pyrolytic laser CVD. Photolytic laser CVD can prepare films without heating substrate only amorphous films, while pyrolytic laser CVD would prepare highly crystallized films. Al_2O_3-TiO_2 system thick films were prepared by laser CVD using CO_2 and Nd:YAG lasers. CO_2 laser is often used for pyrolytic laser CVD. Nd:YAG laser has higher photon energy than CO_2 laser. Nd:YAG laser may fundamentally yield pyrolytic laser CVD; however, the difference of deposition feature between CO_2 and Nd:YAG laser has never been studied.

Chapter 2 Preliminary investigation

In this chapter, the discovery, property and research status of Al_2O_3-TiO_2 system thick films preparation is reviewed. Various film-preparation techniques including sol-gel, pulsed laser deposition, magnetron sputtering and metalorganic chemical vapor deposition (MOCVD) have been developed for preparation of Al_2O_3-TiO_2 system thick films. The main issues for the above preparation techniques are the relatively low deposition rate (R_{dep}). In practical application, high speed preparation of Al_2O_3-TiO_2 system thick films is required. Laser CVD could be an effective approach to prepare high quality Al_2O_3-TiO_2 system thick films at high deposition rate. In the present study, laser CVD was employed to prepare Al_2O_3-TiO_2 system thick films on yttria-stabilized zirconia (YSZ) substrate.

Chapter 3 Preparation of TiO_2 films by laser CVD

This chapter depicted preparation of TiO_2 films on polycrystalline yttria-stabilized zirconia (YSZ) substrate by laser CVD using CO_2 and Nd:YAG lasers. The effects of deposition conditions (chamber total pressure: P_{tot}, deposition temperature: T_{dep}) and laser wavelength on the orientation, phase and microstructure of TiO_2 films were investigated. By using CO_2 laser, single-phase rutile films were obtained independent of P_{tot} and T_{dep}. The microstructures of single-phase (100)-oriented rutile films changed from dense columnar to fully dense structure with increasing T_{dep}, and exhibited faceted morphologies (Fig. 1(a)). The maximum temperature decreased from 1071 to 913 K with increasing P_{tot} from 0.2 to 0.8 kPa. The R_{dep} of rutile reached 92.5 μm h^{-1}. By using Nd:YAG laser, phase of TiO_2 films changed from (100)-oriented rutile to (001)-oriented anatase with increasing T_{dep} and P_{tot}, and their microstructure changed from dense to feather-like to cauliflower-like structure (Fig. 1(b)). R_{dep} increased with T_{dep} up to about 1050 K. The highest value R_{dep} of rutile was 142 μm h^{-1}. The R_{dep} for single-phase anatase film reached 50 μm h^{-1}. this is about 5–1000 times higher than that of TiO_2 by conventional MOCVD. Anatase was stabilized by size effect in the cauliflower-like structure even at high T_{dep}.

High-speed deposition (up to 5000 μm h^{-1}) of TiO_2 films was achieved by laser CVD using CO_2 and YAG lasers at the high vaporization temperature. By using CO_2 laser, phase of TiO_2 films changed from single-phase rutile to mixture phases of anatase and rutile with increasing T_{dep}. The microstructure of TiO_2 films changed from thick columnar to dendritic structure with increasing T_{dep}. By using Nd:YAG laser, phase of TiO_2 films changed from mixture phases of anatase and rutile to single-phase rutile with increasing T_{dep}, and their microstructure changed from dendritic-like structure to solid with increasing T_{dep}. Anatase formed with dendritic and cauliflower-like structures, implying that anatase is stabilized by a size effect of fine grains in the films.

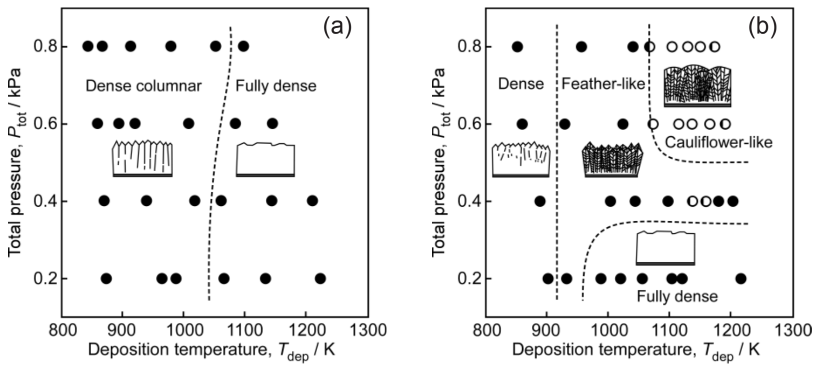

Fig. 1 Effect of T_{dep} and P_{tot} on the phase and microstructure of TiO_2 films prepared using (a) CO_2 laser; (b) Nd:YAG laser. Filled, half-filled and opened circles indicate the rutile mixture and anatase formation.

Chapter 4 Preparation of Al_2O_3 films by laser CVD

In this chapter, Al_2O_3 films were prepared on polycrystalline yttria-stabilized zirconia (YSZ) substrate by laser CVD using CO_2 and Nd:YAG lasers. The effects of deposition conditions and laser wavelength on the phase and microstructure of Al_2O_3 films were investigated. By using CO_2 laser, at T_{dep} = 850-890 K, the microstructure of mixture α- and γ-Al_2O_3 films showed cauliflower-like structure independent of P_{tot}. The morphology of α-Al_2O_3 films changed from a dense columnar structure to a fully dense structure with increasing T_{dep} from 890 to 1250 K independent of P_{tot} (Fig. 2(a)). By using Nd:YAG laser, at T_{dep} = 820-1100 K and P_{tot} = 0.2-0.4 kPa, α-Al_2O_3 films were hexagonal plate-like grains with a columnar structure. At T_{dep} = 840-1200 K and P_{tot} = 0.6-0.8 kPa, Low-temperature phase of γ-Al_2O_3 films were formed. Morphologies of γ-Al_2O_3 films showed a cauliflower-like structure, implying that γ-Al_2O_3 is stabilized by a size effect of fine grains in the films (Fig. 2(b)).. γ-Al_2O_3 films were obtained at high T_{dep}, because of nucleation in a gas phase. The deposition rate of α-Al_2O_3 films were 5-55 μm h^{-1} and 12-68 μm h^{-1} using CO_2 and Nd:YAG laser, respectively. Deposition rate for α-Al_2O_3 films prepared using Nd:YAG laser was slightly higher than that using CO_2 laser.

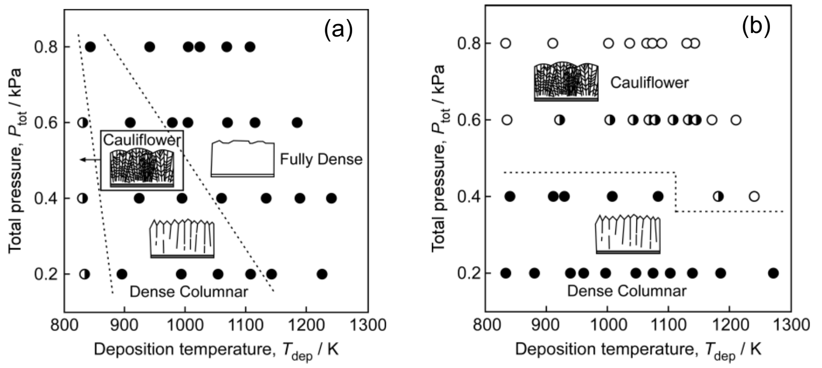

Fig. 2 Effect of T_{dep} and P_{tot} on the phase and microstructure of Al_2O_3 films prepared using (a) CO_2 laser; (b) Nd:YAG laser. Filled, half-filled and opened circles indicate the α-Al_2O_3 and mixture of α- and γ-Al_2O_3 formation.

Chapter 5 Preparation of Al_2TiO_5 films by laser CVD

In this chapter, Al_2TiO_5 films were prepared on polycrystalline YSZ substrate by laser CVD using CO_2 and Nd:YAG lasers. Effect of T_{dep}, $R_{Al/Ti}$ and laser wavelength on crystal phase, orientation and microstructure of Al_2TiO_5 films were investigated. By using CO_2 laser, at lower deposition temperatures (T_{dep} < 800 K), amorphous Al_2O_3 films were obtained. Single-phase Al_2TiO_5 films were formed at $R_{Al/Ti}$ = 1.7-2.0 and T_{dep} = 873-925 K. With increasing of T_{dep}, (130)-oriented Al_2TiO_5 films can be obtained at $R_{Al/Ti}$ = 2.0 and T_{dep} = 925 K. (440)-oriented γ-Al_2O_3 were prepared at rich Al precursor ($R_{Al/Ti}$ = 7.14) (Fig. 3(a)). By using Nd:YAG laser, at lower deposition temperatures (T_{dep} < 780 K), amorphous Al_2O_3 films were obtained. Single-phase Al_2TiO_5 films were formed at $R_{Al/Ti}$ = 1.4-2.1 and T_{dep} = 1085-1090 K. (224)-oriented Al_2TiO_5 films can be obtained at $R_{Al/Ti}$ = 2.11 and T_{dep} = 1086 K. (440)-oriented γ-Al_2O_3 films were obtained at $R_{Al/Ti}$ = 1.32-7.85 and T_{dep} = 821-987 K (Fig. 3(b)).

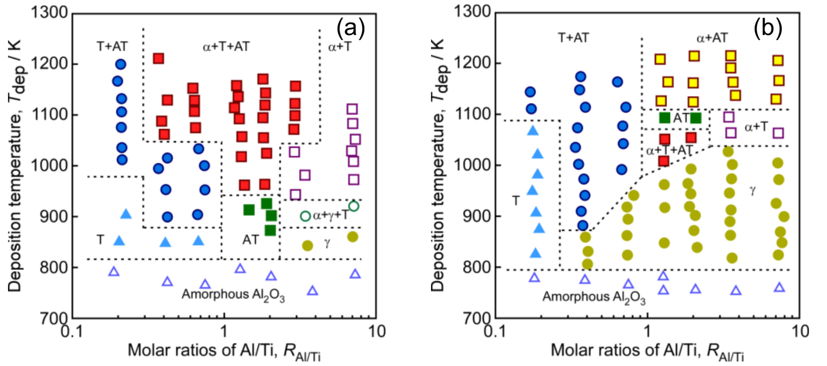

Fig. 3 Effect of T_{dep} and $R_{Al/Ti}$ on the phase and microstructure of Al-Ti-O films prepared using (a) CO_2 laser; (b) Nd:YAG laser. (AT: Al_2TiO_5, α: α-Al_2O_3, γ: γ-Al_2O_3, T: TiO_2)

Chapter 6 Summary

This thesis studied the preparation of Al_2O_3-TiO_2 system thick films (TiO_2, Al_2O_3 and Al_2TiO_5) by laser CVD on YSZ substrate using CO_2 and Nd:YAG lasers. Effect of deposition parameters on the crystal phase, microstructure and orientation of Al_2O_3-TiO_2 system thick films were investigated. By using CO_2 laser, fully dense films (TiO_2 and Al_2O_3) can be obtained at high T_{dep} = 900-1300 K. Growth processing of dense TiO_2 and

Al_2O_3 films can be summarized by lateral growth. By using Nd:YAG laser, Columnar films (TiO_2 and Al_2O_3) can be obtained at T_{dep} = 800-1200 K. Growth processing of columnar TiO_2 and Al_2O_3 films can be summarized by two-dimensional nucleation. Low-temperature phase (anatase, γ-Al_2O_3) was formed by homogeneous nucleation in gas phase at high T_{dep}. Laser beam was scattered by nuclei in gas phase at the region of anatase and γ-Al_2O_3 formation. Low-temperature phases were stabilized by a size effect of fine grains even at high T_{dep}.

論文審査結果の要旨

本論文は、レーザー気相化学析出 (LCVD: laser chemical vapor deposition) 法において、CO_2 および Nd:YAG レーザーを用いて TiO_2、Al_2O_3 および Al_2TiO_5 を合成し、合成条件が、膜の結晶相、配向性および微細構造に与える影響を調べることにより、レーザー波長が LCVD プロセスに与える効果を明かにすることを目的とした研究であり、全 6 章からなる。

第 1 章および第 2 章では、研究の背景を述べ、本論文の目的と構成を記した。

第 3 章では、LCVD により TiO_2 膜を種々の条件で合成し、成膜条件が膜の結晶相、配向性および微細構造に与える影響について調べた。二種類のレーザー、Nd:YAG レーザーおよび CO_2 レーザーを用い、Ti(O*i*Pr)$_2$(dpm)$_2$ (dpm: dipivaloylmethanate) を原料とし、原料気化温度を 473 から 673 K、炉内圧力を 0.2 から 0.8 kPa の範囲内で変化させた。基板には、多結晶 AlN を用いた。CO_2 レーザーを用いた場合、いずれの成膜条件においても緻密なルチル相 TiO_2 膜が得られた。ルチル相 TiO_2 は、(100) 面に配向した。Nd:YAG レーザーを用いた場合、低成膜温度・低炉内圧力域では、(100) 配向のルチル相 TiO_2 が生成したが、高成膜温度・高炉内圧力域では、低温相であるアナターゼ相 TiO_2 が生成した。Ti 原料気化温度 673 K では、成膜速度は 5000 $\mu m\ h^{-1}$ に到達し、従来の CVD 法およびスパッタなどの気相蒸着法よりも数百から数千倍速い成膜速度で TiO_2 膜を合成できた。Nd:YAG レーザーを用いて合成したアナターゼ相 TiO_2 膜は、微細な結晶粒からなるカリフラワー状組織をしていた。

第 4 章では、二種類のレーザーを用いた LCVD により Al_2O_3 膜を種々の条件で合成し、Al(acac)$_3$ (acac; acetylacetonate) を原料とし、炉内圧力を 0.2 から 0.8 kPa の範囲内で変化させ、成膜条件が膜の結晶相、配向性および微細構造に与える影響について調べた。CO_2 レーザーを用いた場合、緻密な柱状晶からなる α-Al_2O_3 膜が得られた。Nd:YAG レーザーを用いた場合、高成膜温度・高炉内圧力域では、微細な結晶粒からなるカリフラワー状組織の γ-Al_2O_3 膜が生成した。これは、気相中で低温相粒子が核生成、サイズ効果によって安定化したためである。

第 5 章では、二種類のレーザーを用いた LCVD により Al_2O_3-TiO_2 系膜を種々の条件で合成し、成膜条件が膜の結晶相、配向性および微細構造に与える影響について調べた。CO_2 レーザーを用いた場合、Al/Ti 比 1.7–2.0 の範囲で Al_2TiO_5 単相膜が得られたが、Nd:YAG レーザーを用いた場合、より広い Al/Ti 比 (1.4–2.1) で Al_2TiO_5 単相膜が得られた。低成膜温度域では、(110) 面に配向した γ-Al_2O_3 膜が生成した。

第 6 章では、本論文を総括した。

本論文により、LCVD 法を用いた Al_2O_3-TiO_2 系膜の合成において、成膜条件およびレーザー波長が膜の結晶相、配向性および微細構造の関係が明らかにすることにより、LCVD の機構に関して新たな知見を与えたもので、学術的および実用的に多大な貢献をしている。

よって、本論文は博士（工学）の学位論文として合格と認める。